ELECTRO-CONDUCTING GLASS-CERAMICS
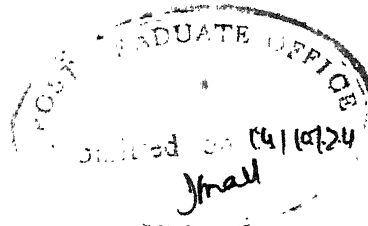
A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
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to the

DEPARTMENT OF METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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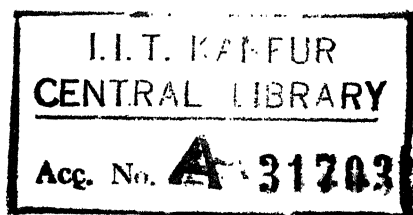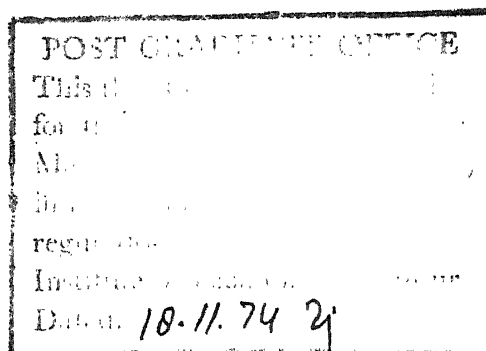
CERTIFICATE

Certified that this work on 'ELECTRO-CONDUCTING GLASS-CERAMICS' by Mr. T. Kaspal Reddy has been carried out under my supervision and that it has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

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SYNOPSIS

ELECTRO-CONDUCTING GLASS-CERAMICS
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NiO-Li$_2$O ceramic samples and Na$^+$ containing silicate glass ceramic samples are prepared. Electrically conducting layers are induced within the surface of the samples using ion exchange and reduction treatments. Conductivity measurements are made as a function of temperature. It is found that it is difficult to induce electrically conducting layers on NiO-Li$_2$O ceramic samples as Na$^+ \rightleftharpoons$ Ag$^+$ diffusion process is very sluggish. Highly conducting layers can be induced even on smooth surfaces (1 micron) of glass ceramic samples. Samples heat treated at 650 $^\circ$C show metallic behaviour with low resistances (around 1 ohm/square) with positive TCR values (around 1000 ppm/$^\circ$K). It is concluded that glass crystal interfaces are helping nucleation of silver droplets to form continuous chains finally. Sample heat treated at 750 $^\circ$C shows typical behaviour of semiconductors with negative TCR and exponential dependence of conductivity on inverse of temperature. It is concluded that discontinuous film of silver droplets cause this behaviour.

CHAPTER I

INTRODUCTION

Because of their potential technical value and scientific
curiosity in the properties of a two dimensional solid, thin
films have been extensively studied over a century. The
technical interests which stimulated these studies have been
rewarded in the form of useful inventions such as a variety of active
and passive microminiaturized components and devices, solar
cells, radiation sources and detectors, magnetic memory devices,
cryotrons, bolometers, interference filters, and reflection and
antireflection coatings. A large number of methods have been
developed to prepare thin films of various materials. Salient
features of some well known methods are discussed below followed
by a brief review of methods used to obtain highly conducting
layers on glasses which are used in printed and integrated
circuitry.

The deposition techniques for thin films may be broadly
classified under three headings: thermal evaporation, cathodic
sputtering and chemical deposition.

1.1 THERMAL EVAPORATION

Solid materials vaporize when heated to sufficiently
high temperatures. The condensation of the vapour onto a
cooler substrate yields thin solid films. The rate of free
evaporation of vapour atoms from a clean surface of unit area

in vacuum is given by the Langmuir expression

$$m_e = 5.83 \times 10^{-2} \, p_e \sqrt{M/T} \quad g/(cm^2)(sec)$$

where p_e ($< 10^{-2}$) is the equilibrium vapour pressure (in Torr) of the evaporant under saturated-vapor conditions at a temperature T, and M is the molecular weight of the vapor species. However, the rate of deposition of the vapor on a substrate depends on the source geometry, its position relative to the substrate and the condensation coefficient. Holland[1] has discussed thoroughly the theoretical distribution of vapor from a point, a wire, a small surface, an extended strip and from cylindrical and ring type of sources.

Thermal evaporation may be achieved directly or indirectly by a variety of physical methods:

(1) Resistive Heating: This method consists of heating the material with resistively heated filament or boat, generally made of refractory metals such as W, Mo, Ta, and Nb, with or without ceramic coatings.

(2) Flash Evaporation: This is a rapid evaporation method used to prepare thin films of multicomponent alloy or compound, which tends to distill fractionally. In this method fine particles of material are dropped continuously onto a hot surface so that numerous discrete evaporations occur.

(3) <u>Arc Evaporation</u>: By striking an arc between two electrodes of a conducting material, sufficiently high temperatures can be generated to evaporate refractory materials such as Nb and Ta.

(4) <u>Exploding Wire Technique</u>: In this technique a wire is exploded by a sudden resistive heating with a transient high current density approaching 10^6 A/cm^2.

(5) <u>Laser Evaporation</u>: The enormous intensity of a laser may be used to heat and vaporize materials by keeping the laser source outside the vacuum system and focussing the beam onto surface of the material to be evaporated.

(6) <u>Induction Heating</u>: The induction heating may be supplied to the evaporant directly or indirectly from the crucible material.

(7) <u>Electron-bombardment Heating</u>: This method consists of a heated W filament to supply electrons which are accelerated by applying a positive potential to the material for evaporation. The kinetic energy of electrons is converted into heat energy which evaporates the material.

1.2 CATHODIC SPUTTERING

The ejection of atoms from the surface of a material (the target) by positive ion bombardment is called cathodic sputtering. The ejected or sputtered atoms can be condensed on a substrate to form a thin film.

Various types of sputtering techniques can be classified into three categories: (1) Glow discharge sputtering, (2) Low pressure sputtering and (3) Reactive sputtering.

A cheap and simple source of ions for sputtering is provided by the well known phenomenon of glow discharge due to an applied electric field between two places (electrodes) in a gas at low pressures. The cathode is covered with the sputtering material, and the anode carries the film substrate. The optimum pressure range for glow discharge sputtering is between 25 and 75 m Torr. This high pressure causes contamination of the film. But rate of deposition can be controlled very easily in this case.

Reasonable sputtering rates at low pressures may be obtained by increasing the ionization of the sputtering gas by (1) increased ionizing efficiency of the available electrons, (2) increased supply of ionizing electrons, and (3) an ion-beam source.

In case of reactive sputtering some reactive gas is used as sputtering gas instead of an inert gas. This enables the deposition of various compounds often not obtainable by vacuum deposition.

An important advantage of the sputtering process is that the composition of a sputtered film is the same as that of cathode. So this process is most useful for multicomponent materials.

1.3 CHEMICAL DEPOSITION

Various chemical deposition methods have been developed
for deposition of thin and thick coatings. These may be
broadly classified into two categories: electro-deposition
and chemical vapor deposition. Both have widespread applications
of major technical and commercial value.

(1) Electro deposition: In this method a suitable electrolyte
of the metal to be deposited is subjected to electrolysis and
the metal ions are reduced to deposit on a substrate. This
reduction can be done either by passing direct current through
electrolyte, in which case the deposition takes place on cathode,
or by chemical methods such as that used in the well known
technique of silvering glass dewars. A protective oxide film
of limited thickness can be formed on metals by anodic polari-
zation of these metals in suitable aqueous solution, which does
not dissolve the oxide.

(2) Chemical vapor deposition: Chemical vapor deposition
involves vaporization of a volatile compound of the substance
to be deposited and the vapor is thermally decomposed or reacted
with other gases, vapors, or liquids at the substrate to yield
nonvolatile reaction products which deposit atomistically on
the substrate.

A comparative summary of various deposition techniques
is given by Chopra[2].

1.4 DEVELOPMENT OF HIGHLY CONDUCTING LAYERS ON GLASSES

A number of methods have been developed for obtaining highly conducting layers on glasses. Conducting layers on glasses can be obtained by two ways: (1) by simply adding a conducting layer to the glass, the latter undergoing no physical or chemical change and (2) by inducing conductivity in a thin layer within the glass surface. The former methods include metallizing procedures wherein platinum, gold[3] or copper salts are heated to reduction on the glass, vaporization of metals onto the surface of glass[4], firing silver oxide or metal powder on with the aid of auxiliary fluxes and painting on lacquers containing flaky metals in suspension.[5]

Blodgett[6,7] developed techniques for inducing conductivity in a thin layer within the surface of glass containing lead oxide and other metal oxides. They treated these glasses in hydrogen leading to reduction of metallic ions within the surface. The reduced metallic ions increased the conductivity of surface. They obtained surface resistances ranging from 100 ohms/square to 10^{10} ohms/square depending on the glass composition.

Ion-exchange and Reduction Technique

Chakravorty[8,9,10] developed a technique to induce high conductivity in a thin layer within the surface of alkali containing glasses. He used Na^+ ion containing silicate glasses

of various compositions in different systems. The process involves two steps: $Na^+ \rightleftharpoons Ag^+$ ion exchange and reduction in hydrogen.

The samples were immersed in molten silver nitrate and held around $330^\circ C$ for about 6 hours. At this temperature $Na^+ \rightleftharpoons Ag^+$ ion exchange takes place. The Ag^+ ions from the molten silver nitrate diffuse into the glass and take the place of Na^+ ions which diffuse out of the glass surface. The extent of diffusion of Ag^+ ions depends on the temperature, time and composition (particularly Na^+ content) and structure of the glass.

The samples are washed in water to remove traces of $AgNo_3$ on samples and held in hydrogen atmosphere diluted by nitrogen around $330^\circ C$ for about 16 hours. After this treatment the samples showed very low surface resistances ranging from 0.15 ohm/square to 4.1 ohm/square depending on the glass composition[10]. The temperature coefficient of resistance (TCR) values were around 2000 ppm/$^\circ$K. Some of these glasses showed memory switching effect[9].

The microstructural studies of the ion exchange and reduced layers confirm that such high surface conductances arise due to the formation of continuous chains of metallic silver droplets in glass matrix. These droplets form due to reduction of silver ions by hydrogen and subsequent nucleation and growth

of silver metal. It was difficult to measure the thickness of
the conducting layers because of the surface roughness which
was necessary for obtaining the high conductance effect. It
is believed that imperfections introduced in the surface by
grinding operation increase the efficiency of nucleation of
metallic particles which can then grow sufficiently to form
a continuous chain.

1.5 ELECTRICAL CONDUCTION IN METAL FILMS

Depending on the growth stages a film may be granular
or islandlike (consisting of discrete particles), porous
(network), or continuous. Each stage has its characteristic
electrical properties.

Electrical conductivity of a granular film is many
orders of magnitude smaller than that of bulk material and is
generally characterized by a negative TCR. The conductivity
is found to vary exponentially with the inverse of temperature,
suggesting that the conduction mechanism is thermally activated.
It is ohmic at low applied fields, but nonlinear at high fields.
Experimental results have been interpreted in terms of various
conduction mechanisms; such as thermionic and Schottky emission,
and tunneling through the vacuum gap and/or via traps in the
dielectric substrate. TCR of both signs and of variable
magnitudes have been observed in discontinuous metal fields.
The exact behaviour of conductivity and TCR depends on the details

of the film microstructure.

Electrical conduction in porous films is due to the particles, and bridges and gaps between the particles and is very sensitive to the physical and electrical changes in the filamentary bridges brought about by aging, annealing, and adsorption. Conductivity of a porous film is less than bulk metal and is largely determined by grain-boundary scattering, diffused scattering at grain surfaces, and intergranular tunneling.

The structure of continuous films is similar to that of bulk metal but for thickness. The conductivity of bulk metal varies with mean free path (mfp) of electrons. As the thickness of a metal film becomes comparable in magnitude with mfp, the film boundaries impose a geometrical limitation on the movement of the conduction electrons and thus effective value of the mfp. This is known as size effect and various theories have been proposed to explain it.

CHAPTER II

STATEMENT OF THE PROBLEM

An important requirement of the materials used as resistors in potentiometers is that their resistance should not vary much in the vicinity of room temperature. Normally the temperature coefficient of resistivity (TCR) should be below 100 ppm/$^{\circ}$K in the range of -100°C to +100°C. Similar requirements are to be fulfilled in case of materials used as conductors in printed circuits wherein thin metallic films are deposited on insulating boards.

In case of wire wound potentiometers it is likely that the wire may break (possibly due to erosion by contact terminal) rendering the instrument useless. By replacing the resistor wire by a thin film on an insulating substrate this problem can be got rid of. However, this thin film should have low TCR. It should be mechanically strong and have smooth surface to enable a contact terminal to slide over it.

The present investigation is aimed at developing and studying electrically conducting films of above mentioned characteristics, on insulating substrates by $R^+ \rightleftharpoons Ag^+$ ion exchange reaction (R^+-any cation) followed by a reduction treatment in hydrogen. Chakravorty induced electrically conducting layers in some alkali containing silicate glasses by subjecting them to $Na^+ \rightleftharpoons Ag^+$ ion exchange reaction followed

by reduction treatment in hydrogen. Most of the glasses gave
large TCR values around 2000 ppm/$^{\circ}$K. They had rough surfaces
(120 mesh) as surface roughness was necessary for obtaining
the high conductivity. Therefore, the present investigation
is aimed at reduction of TCR values as well as surface roughness
in the conducting layers.

Because of opposing trends of variation of resistance
with temperature of metals and semiconductors a suitable metal-
semiconductor multiphase system is likely to give a low value
of TCR. NiO in solid solution with Li_2O shows semiconducting
characteristics having low values of bulk resistivity at room
temperature.[11,12] By subjecting such a ceramic sample to $Li^+ \rightleftharpoons Ag^+$
ion exchange reaction and subsequent reduction of the surfaces
in hydrogen it may be possible to induce electrically conducting
layers of low TCR. The positive variation with temperature
of resistance of silver droplets and negative variation with
temperature of resistance of oxide semiconductor may compensate
to give a low TCR value. Therefore, $NiO-Li_2O$ ceramic system
is selected for the present study.

If smooth surfaces of alkali containing silicate glasses
are ion-exchanged with silver and are subsequently reduced,
high conductivity cannot be induced on such glass surfaces.[10]
If some crystals are precipitated in the glass phase the glass-
crystal interfaces may act as nucleation sites and help the

nucleation of silver droplets. This may be achieved by starting with glass-ceramic samples instead of glass samples. Therefore, it is proposed to induce and study electrically conducting layers on glass ceramic samples of silicate glasses with alkali ions.

To summarize, the objectives of the present investigation are to induce and study electrically conducting layers, using ion exchange and reduction technique, on

(1) $NiO-Li_2O$ ceramic system

and (2) Alkali containing silicate glass ceramic systems.

CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 PREPARATION OF CERAMIC SAMPLE

It is proposed to study the modified surfaces of
20 Li_2O, 80 NiO (Mol %) ceramic sample. Lithium containing
NiO ceramic is a known semiconductor and lithium content is
kept high in order to ensure a fairly high concentration of
silver ions at the surface after $Li^+ \rightleftharpoons Ag^+$ ion-exchange reaction.

3.1.1 Batch Composition

Li_2O is taken as Li_2CO_3 and NiO as $NiCO_3.2Ni(OH)_2.4H_2O$.
Both are reagent grade materials. Required weights of materials
for 20 Li_2O 80 NiO sample are weighed into a porcelain mortar
and ground thoroughly under acetone, with a pestle. The batch
is then dried in an oven and transferred into a sillimanite
crucible.

3.1.2 Calcination

The batch in the crucible is calcined at $700^\circ C$ for two
hours in a wire wound muffle furnace. During calcination the
carbonates and hydroxides decompose and CO_2 and H_2O escape from
the batch leaving pure oxides in the crucible. The colour of
the powder changes from green to black. The batch is then
transferred into mortar and ground well under acetone. After
drying the batch is ready for pressing.

3.1.3 Pressing

The batch is pressed into pellets using a split die and punch made of high speed steel. Pressure is applied by a hydraulic press.

Pressure applied 10^5 psi

Pellet size   : 1/2" dia x 1/4" thick.

3.1.4 Sintering

The pellets are placed on a platinum foil which is then introduced into a horizontal tube furnace heated by globars. The pellets are sintered at 1350°C for 24 hours.

3.2 PREPARATION OF GLASS CERAMIC SAMPLES

It is proposed to study the modified surfaces of glass ceramic samples. Glasses of various compositions are melted and tried for crystallization at various temperatures and for various times. No special nucleating agents are added. However, Bi^{3+} ions present in glass may reduce at high temperature to form bismuth droplets which may act as nucleating agents.

3.2.1 Batch Composition

Twelve glass compositions have been tried in this investigation. The compositions of glasses are given in Table I. Sodium and calcium are introduced as carbonates and all other components as their respective oxides. All of them are of reagent grade. Required quantities of chemicals,

TABLE I

Composition of Glasses (Mol %)

Glsss No.	SiO_2	Na_2O	CaO	Bi_2O_3	B_2O_3	Al_2O_3	Sb_2O_3	PbO
1	55	25	10	10				
2	45	25	20	10				
3	60	18	14	8				
4	55	18	17	10				
5	55	11	33	1				
6	50	18	22	10				
7	50	25		7	18			
8	64	10		8	18			
9	56	27		7	10			
10	55	30		8		7		
11	56	27			10		7	
12	56	27			10			7

for 100 grams glass, are weighed into a mortar and mixed thoroughly under acetone to get a homogeneous mixture of the components.

3.2.2 Glass Melting

The mixed batch is transferred to alumina crucible which is then kept in a pit type glass melting furnace heated by silicon carbide heating elements. This furnace with necessary details is shown in Figure 1. The alumina crucible is kept inside a sillimanite crucible filled with alumina powder, in order to protect heating elements from molten glass coming out of alumina crucible due to breakage, overflow etc. The batch is first heated slowly to $900^{\circ}C$ to $1000^{\circ}C$, depending on composition, to allow the calcination of components. The carbonates decompose and carbon dioxide escapes in this stage. The batch is held at $900^{\circ}C$ to $1000^{\circ}C$ for 1 to 2 hours to dissolve all the components. Then the temperature is raised to $1200^{\circ}C$ to $1300^{\circ}C$ relatively fast and held there for a period extending from half an hour to one hour to refine the glass, eliminate gas bubbles and make the glass fluid. The molten glass is then cast into 0.8 x 2 x 10 cm plates using aluminium moulds. As soon as the glass becomes like a solid mass, it is transferred to annealing furnace held at $400^{\circ}C$ to $450^{\circ}C$. After keeping the glass at this temperature for one to two hours, the power is put off and the glass is cooled in the furnace to room temperature.

A - Furnace shell

B - Hot face insulation bricks

C - SiC heating elements (six nos.)

D - Thermocouple

E - Lid

F - Viewing port

H - Sillimanite crucible

J - Alumina powder

K - Alumina crucible

L - Glass batch

Fig. 1 - Glass melting furnace.

The most important precaution to be taken in the preparation of glass ceramic samples is to avoid crack formation in the sample. Even fine cracks lead to rejection of sample. Because the ion-exchange reaction opens these cracks and connects electrically conducting layers on opposite sides of the sample. Therefore, rapid heating and cooling of the sample at all stages of sample preparation are avoided.

3.2.3 Heat Treatment

From the annealed glass plate 0.8 x 1 x 2 cm size pieces are cut with a diamond cut-off wheel. The samples are heated in a muffle furnace to selected temperatures for selected times and cooled in the furnace to room temperature. During this treatment the glass samples crystallize. Transparent glass finally becomes opaque after crystallization. Various temperatures upto melting temperature range and various periods of times upto 12 hours are tried to crystallize as many types of glasses as possible.

3.3 ION-EXCHANGING TREATMENT

The glass-ceramic samples are subjected to $Na^+ \rightleftharpoons Ag^+$ ion-exchanging treatment and ceramic samples to $Li^+ \rightleftharpoons Ag^+$ ion-exchanging treatment. Ag^+ ions are supplied from a molten bath of silver nitrate in which the sample is immersed.

The surfaces of the sample are ground flat in silicon carbide grit of mesh sizes between 120 and 600. Some samples

are polished with 1μ alumina powder on polishing wheel.

The glass-ceramic sample is placed in a pyrex glass crucible of size 3/4" dia x 1" ht and the empty space is filled with reagent grade silver nitrate. The crucible is placed in a nickel crucible and introduced into the tube furnace used for reduction work. As the temperature of the furnace is raised silver nitrate melts and $Na^+ \rightleftharpoons Ag^+$ ion-exchange takes place. This ion-exchange reaction treatment is given at $330^\circ C$ for five hours in case of glass ceramic samples and at $350^\circ C$ for 12 hours in case of $NiO-Li_2O$ ceramic samples. After the treatment is over the nickel crucible is taken out of the furnace, the sample is taken out of molten silver nitrate and immediately it is introduced into the furnace. The sample is cooled to room temperature in the furnace. This precaution avoids formation of cracks due to thermal stresses. The cooled sample is washed in water to remove the traces of silver nitrate solidified on the surfaces of samples. Now the samples are ready for reduction treatment.

3.4 REDUCTION TREATMENT

The ion-exchanged samples are reduced in hydrogen atmosphere diluted with nitrogen. The experimental set up for this treatment is shown in Figure 2. The samples are placed over a refractory base introduced into a pyrex glass tube. The tube is inserted into a wire wound horizontal tube furnace. The

A – Furnace
B – Mullite tube
C – Pyrex glass tube
D – Thermocouple
E – Inlet for N+H gas mixture
F – Outlet for N+H gas mixture
G – Refractory base

J – T joint to mix H₂ and N₂
K – Flow meter for hydrogen
L – Flow meter for nitrogen
M – Calcium chloride
N – Conc. H₂SO₄
P – Pyrogallol acid
H – Sample

Fig. 2 – Experimental set-up for reduction treatment.

ends of the tube are closed with rubber stoppers with holes drilled in them. The hydrogen-nitrogen gas mixture enters the tube from one side and leaves from the other. A thermocouple is inserted into the glass tube to control and measure the temperature of samples. Nitrogen gas is purified by passing it through alkaline solution of pyrogallol acid (to absorb oxygen), concentrated sulphuric acid (to absorb moisture) and calcium chloride (to absorb moisture). Purified nitrogen and hydrogen are mixed by a 'T' joint and passed on to the samples. The flow rates of both the gases are indicated by flowmeters connected in the gas flows.

For all the experiments the gas flow rate is 100 cc per minute of H_2 and 1000 cc per minute of N_2. The temperature and time of reduction are $330^{\circ}C$ and 16 hours respectively.

3.5 RESISTANCE MEASUREMENT

The surface resistance of the samples is measured from $-150^{\circ}C$ to $200^{\circ}C$ by four terminal method.

3.5.1 Sample Preparation

All the six surfaces of the sample are ion-exchanged and reduced. These surfaces are high conducting compared to the bulk of the sample. Only one surface is needed for surface resistance measurement. Therefore, the remaining conducting surfaces are removed to avoid parallel paths of current. This is done by grinding off these surfaces in SiC grit.

Finally, one rectangular conducting surface is preserved for surface resistance measurement.

Four electrodes are painted on the test surface with silver paint. Thin copper wires are cemented on to the electrodes with silver paste. The separation between central electrodes is about 1 - 3 mm. The width of electrodes is same as that of test surface. The electrodes are cured by drying the sample in oven at $80^{\circ}C$.

3.5.2 Electrical Circuit

The electrical circuit used for the measurement of surface resistance is shown in Figure 3. Direct current is passed through the extreme electrodes which are connected to a D.C. power supply. Current is determined by reading directly from milli-ammeter or by measuring voltage drop across a standard resistor. Both are connected in series with the sample. Voltage drop between central electrodes is measured with a potentiometer. The slope of the plot of voltage against current gives the resistance of the surface between central electrodes. The surface resistance of the sample is given by the relation

$$R = \beta \frac{l}{b}$$

where R is the resistance of the surface between central electrodes (ohms), l is the separation between central electrodes (cm), b is the width of central electrodes (cm) and β is the

Fig. 3 – Electrical circuit for resistance measurement.

surface resistance of test surface (ohms/square). Since the voltage is measured by null balance method the effect of contact resistance of electrodes is eliminated.

The temperature coefficient of resistance (TCR) is calculated by using the relation

$$TCR = \frac{1}{R_{20}} \frac{dR}{dT}$$

where $\frac{dR}{dT}$ is the slope of resistance versus temperature plot and R_{20} is the resistance at $20^{\circ}C$.

3.5.3 Resistance Measurement above Room Temperature

Resistance measurement above room temperature is made by heating the sample in the tube furnace shown in Figure 2. The sample holder used for this purpose is made of hot face insulation brick and serves two purposes- holding the sample and closing one end of the furnace. The temperature is maintained constant at $10-15^{\circ}C$ intervals and at each temperature voltage-current (V-I) plot is obtained. From these plots the resistances are determined. The temperature at each level remains constant within $\pm 0.5^{\circ}C$.

3.5.4 Resistance Measurement below Room Temperature

Resistance measurement below room temperature is made with the use of a nitrogen gas flow cryostat shown in Figure 4. The sample is cooled by controlled flow of nitrogen vapors from liquid nitrogen.

Fig. 4 -Experimental set-up for measurement of surface resistance below temperature.

The liquid nitrogen is held in a dewar with a narrow neck. A 1" diameter teflon tube is sealed to the dewar in vertical position. The sample is held in a sample holder which is inserted into lower half of the tube by an aluminum rod which, in turn, is fixed at the top of the tube. The lead wires and thermocouple wires come out from the top end of the tube. The tube is closed completely leaving a small hole at the top for the escape of nitrogen vapors. A kanthal wire heater is introduced into the liquid nitrogen for boiling liquid nitrogen. The vapors from liquid nitrogen pass over the sample, cool it and escape through the hole provided at the top of the tube. By controlling the power given to the heater the rate of vaporization can be controlled, which, in turn, controls the temperature of the sample. With this set up the sample can be cooled to $-200^{\circ}C$ and temperature can be maintained constant at any level within an accuracy of $\pm 1^{\circ}C$. Provision is made to add liquid nitrogen into the dewar at intermediate stages. V-I plots are taken at different levels of temperature of $15^{\circ}C$ interval.

3.6 DETERMINATION OF THICKNESS OF CONDUCTING LAYERS

A successful attempt is made to find the thickness of conducting layer. For this the surface resistance of the test surface is measured as a function of thickness of conducting layer. The surface is ground off in steps of 5 to 10 microns

and room temperature resistance is found at each step. This is continued until the surface resistance shoots to that of virgin glass ceramic sample.

Thin layers from the test surface are removed by polishing on a polishing wheel with one micron alumina powder. A special sample folder shown in Figure 5 is used for this purpose. This is made of stainless steel and consists of two parts. One part is a hollow cylinder with its diameter at one end larger than at other end. The other part is a solid cylinder closely fitting into the hollow cylinder. The sample is attached to the lower end of solid cylinder using wax, as shown in the figure. With this arrangement the test surface of the sample can be maintained horizontal and can be polished off uniformly within ± 1 micron.

The test surface is attached to the sample holder and the opposite surface is ground in SiC grit to make it perfectly parallel to the test surface. Now the new surface is attached to the sample holder and test surface is polished on polishing wheel for a few minutes. The difference in thickness of the sample is found with micrometer with least count of one micron. The surface resistance is found as described before.

3.7 MICROSCOPIC EXAMINATION OF SAMPLES

The NiO-Li$_2$O ceramic and glass ceramic samples are prepared for microscopic examination by grinding in SiC grit

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A – Outer hollow cylinder

B – Inner cylinder

C – T end of inner cylinder

D – Screw

E – Polishing wheel

F – Sample

Fig 5 –Sample holder for polishing.

and polishing on polishing wheel with 0.05 micron alumina
powder. The micrograph of polished NiO-Li$_2$O ceramic sample
is taken to examine porosity, using an optical microscope.
The glass ceramic samples are etched with 10 % hydrofluoric
acid and their micrographs are taken to examine various phases
present in them.

3.8 X-RAY DIFFRACTION STUDY

The X-ray diffraction pattern of virgin glass ceramic
sample is taken to identify the crystalline phase.

CHAPTER IV

RESULTS

4.1 NiO-Li$_2$O CERAMIC SAMPLE

Various experimental data and results of NiO-Li$_2$O ceramic sample are summarized in Table II. The high strength needed to break the sintered sample and high linear shrinkage (21 %) show that the samples are sintered well. But porosity seems to be high as revealed by the microstructure of virgin sample polished to 0.05 micron and unetched (Figure 22).

All the samples are given ion-exchange and reduction treatments under identical conditions. But some samples are given an additional water treatment after ion-exchanging but before reduction. These samples are immersed in water for about 8 hours. Some white powder came out of the surface and deposited on the bottom of the beaker containing the water. This powder appears to consist of silver nitrate. This can be confirmed by X-ray analysis. This sample after reduction treatment has surface resistance of about 10^8 ohms/square, which is equal to that of virgin sample. The black colour of virgin sample remains the same after reduction also. This means that ion exchange and reduction treatments do not improve the surface conductivity of the ceramic sample.

However, those samples which are not given additional water treatments have very low surface resistances of 0.3101 ohms/sq.

TABLE   II

Experimental Data and Results of NiO-Li$_2$O Ceramic Sample

1. Composition (mole %)   : 80 NiO, 20 Li$_2$O

2. Calcination   : 700 $^{\circ}$C, 2 hours

3. Pressing   : Pressure- 10^5 psi

Size of pellet- .5" dia x .25" thickness

4. Sintering   : 1350 $^{\circ}$C, 24 hours

5. Linear Shrinkage   : 21 %

6. Surface roughness   : 120 mesh

7. Ion-exchange   : 350 $^{\circ}$C, 12 hours

8. Reduction   : 350 $^{\circ}$C, 16 hours

9. Surface Resistance   : 10^8 ohms/square for virgin sample.

: 10^8 ohms/square for modified sample with water treatment.

: 0.3101 ohms/square for modified sample without water treatment.

10. TCR   : 3300 ppm/$^{\circ}$K for modified sample without water treatment.

The surface has silver whitish colour. This high conductivity is probably due to the reduction of Ag^+ ions deposited in the pores exposed to the surface. The TCR of conducting layer is 3300 ppm/^{o}K which is of the same order of magnitude as that of bulk silver (3800 ppm/^{o}K). This fact also supports the argument that high conductivity is due to reduction of Ag^+ ions deposited in pores exposed to the surface. In case of water treatment these are probably removed out of the pores in the form of white powder.

Figure 6 shows the temperature variation of surface resistance of the sample with no water treatment. The resistance values are obtained from the slopes of voltage current (V-I) plots at each temperature. These plots are found to be straight lines passing through the origin. Two of such plots are shown in Figure 7. Current voltage values at various temperatures are given in Appendix I. Accurate values of slopes of V-I plots are obtained by fitting the points to a straight line by least square method using a digital computer. The programme for this purpose is shown in Appendix IX.

4.2 CLASS CERAMIC SAMPLE

Various experimental data and results of the glass ceramic sample are summarized in Table III.

4.2.1 Crystallization

Crystallization is observed in only two glass compositions (glass nos. 1 and 2 in Table I) of twelve glasses melted.

Fig. 6 – Resistance variation with temperature of
NiO–Li$_2$O ceramic sample.

Fig. 7 – V-I Characteristics of NiO – Li$_2$O ceramic sample.

TABLE III

Experimental Data and Results of Glass Ceramic Samples

Sample No.	Composition Mol %	Heat Treatment Temp. °C	Time hrs.	Surface rough-ness	Surface resistance at 20 °C β_{20} ohms/sq.	TCR ppm/°K	Thickness of conducting layer (micron)
1A1μ	$55SiO_2, 25Na_2O$ $10 Bi_2O_3, 10CaO$	650	2	1μ	28.09	684	17
1A600	– do –	650	2	600 (mesh)	0.7336	1324	30
2A1μ	$45SiO_2, 25Na_2O$ $10 Bi_2O_3, 20CaO$	650	2	1μ	0.766	985	
2A600	– do –	650	2	600 (mesh)	0.268	1340	
1B600	$55SiO_2, 25Na_2O$ $10 Bi_2O_3, 10CaO$	750	2	600 (mesh)	3.55×10^5	–4340	

Note:

(1) The first digit in sample number refers to glass number given in Table I, next letter refers to heat treatment given (A– 650 °C, 2 hours; B– 750 °C, 2 hours) and last number refers to surface numbers.

(2) Surface resistance of all virgin samples is more than 10^9 ohms/square.

(3) Ion Exchange treatment for all samples: 330 °C, 5 hours.

(4) Reduction treatment for all the samples: 330 °C, 16 hours. 100 cc of H_2 + 1000 cc of N_2 per minute.

Compositions with high CaO content (more than 20 mol °/o) are
found difficult to melt to give a homogeneous glass. No cryst-
allization is observed in the remaining glasses in the range
from room temperature to around 1000 °C. In glasses 1 and 2
the crystallization is found to occur throughout the bulk of
the sample. The samples are crystallized at a given temperature
for various times and the broken pieces are observed. At all
times the crystallization is found to be throughout the entire
volume of samples. X-ray diffraction pattern of glass ceramic
(composition 1) is shown in Figure 21. It shows distinct lines
of diffraction confirming the presence of crystalline phase.
However, the exact crystal could not be identified as the lines
do not conform to any standard crystal. The micro-structures
of glass ceramics of composition 1, heat treated at 650 °C and
750 °C are shown in Figure 23. The crystal boundaries are not
very clear. However, it appears that the sample heat treated
at 650 °C consists of large number of small crystals (about
2 microns) in glass matrix and that heat treated at 750 °C
consists of small number of large crystals (10 - 20 microns)
occupying greater volume of the bulk of the sample. The
crystals in latter case seem to touch each other.

Only glasses 1 and 2 are crystallized, ion exchanged,
reduced and various studies are made. The experimental data
and results are summarized in Table III. All the samples are
given the same ion exchange and reduction treatment in order to

compare meaningfully the effect of glass composition, heat treatment and surface roughness on the properties of induced conducting layers.

4.2.2 Surface Resistance

Surface resistance of the samples is measured by taking the V-I plots at various temperatures. These are given in Appendices II to VI. These plots are found to be straight lines passing through the origin. Some of these plots for each sample are shown in Figures 9, 11, 13, 15, 17. Accurate values of slopes (that is, resistance values) are determined by fitting the points to a straight line by least square method using a digital computer. The programme used for this purpose is shown in Appendix IX. The surface resistances are found to be very low, of the order of 1 ohm/square, indicating that the modified surfaces are highly conducting. But the sample heat treated at higher temperature (750 $^{\circ}$C) is found to show high resistance of the order of 10^5 ohms/square which is in the range of semi-conduction. Rough surfaces are found to show lower resistance than smooth surfaces as indicated in Table III.

4.2.3 Temperature Coefficient of Resistance

For all the samples the resistance is found as a function of temperature. Resistance is plotted against temperature. All the samples heat treated at lower temperature (650 $^{\circ}$C) are found to show linear relationship with positive TCR as shown in Figures 8, 10, 12, 14. Obviously, these samples show metallic conduction.

Rough surfaces are found to show larger TCR values than smooth surfaces as indicated in Table III. But the sample heat treated at higher temperature (750 $^{\circ}$C) is found to show an exponential dependence of conductivity on inverse of temperature as shown in Figure 18. The resistance decreases as temperature increases as shown in Figure 16, conforming to the typical behaviour of semiconductors.

4.2.4 Thickness of Conducting Layers

Surface resistance at room temperature is measured as a function of thickness of conducting layer removed. The data are given in Appendices VII and VIII. Resistance is plotted against thickness removed. Figures 19 and 20 show such plots for samples 1A1μ and 1A600 respectively. The resistance increases very rapidly with thickness of conducting layer removed. The thickness of conducting layer of sample 1A1μ is found to be 17 microns and that of sample 1A600 is found to be 30 microns. From the Figures 19 and 20 it is obvious that thickness of conducting layer of rough surface is more than that of smooth surface.

Fig. 8 – Resistance variation with temperature of sample 1A1μ.

Fig. 9 – V-I Characteristics of sample 1A1μ.

Fig. 10.—Resistance variation with temperature of sample 1A600.

Legend: During cooling, During heating

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Fig. 11 – V–I Characteristics of sample 1A600.

Fig. 12 – Resistance variation with temperature of sample 2A1μ.

Fig. 13 – V-I Characteristics of sample 2A1µ.

Fig.14 –Resistance variation with temperature of
sample 2A 600.

Fig. 15 – V-I Characteristics of sample 2A600.

Fig.16 – Resistance variation with temperature of sample 1B600.

Fig. 17 - V-I Characteristics of sample 1B 600.

Fig. 18 – Log σ vs. 1/T for sample 1B600.

Fig. 19 –Resistance variation with thickness of conducting layer removed of sample 1A1μ.

Fig. 20-Resistance variation with thickness of conducting layer removed, of sample 1A 600.

Temperature of measurement = 32.5°C
l = 0.5 cm
b = 0.85 cm

Fig. 21.- X-ray diffraction pattern of glass-ceramic sample.

FIG. 22   Microstructure of 80MgO - 20Li₂O Sample. Polished
with 0.05 micron alumina powder and unetched. Dark
areas are pores. Magnification 400 X.

A

B

Fig. 23   Micro-structures of glass-ceramic samples of
composition - 1,A - heat treated at 650°C,

CHAPTER V

DISCUSSIONS

5.1 NiO-Li$_2$O CERAMIC SAMPLE

The effect of water treatment on the surface resistance and TCR value of NiO-Li$_2$O ceramic samples after ion exchange and reduction treatments shows that it is difficult, if not impossible, to obtain high conducting layers on the surface of NiO-Li$_2$O ceramic samples. This can be attributed to one or both of the following reasons.

(1) Extremely slow Li$^+$⇌Ag$^+$ ion exchange reaction rate

(2) Extremely slow rate of nucleation and growth of silver droplets.

Both the factors depend on the diffusion coefficient of Ag$^+$ and Li$^+$ ions in the ceramic sample. The ceramic sample is crystalline. Therefore, the diffusion must take place either by vacancy motion or interstitial motion. The diffusion process by this method is very slow compared to that in glass phase in which the atoms are packed loosely. Therefore, ion exchange and reduction treatments induce conducting layers in glasses but not on ceramic samples.

Nucleation and growth of silver phase during reduction is also diffusion controlled. For the formation of critical nucleus of silver, the silver atoms should diffuse to form a cluster of critical size. Further growth takes place by the

diffusion of more ions towards critical nucleus. As these diffusion processes are very sluggish in crystalline matrix, and available number of silver ions is also very low (due to sluggish ion exchange reaction), it is very difficult to obtain dispersion of silver droplets in ceramic matrix.

Therefore, it appears that metallic droplets cannot be formed in crystalline semiconducting matrix by ion exchange and reduction treatments.

5.2 GLASS CERAMIC SAMPLE

The rate of nucleation and growth of crystals in glass is dependent on temperature as shown in Figure 24. Any glass crystallized around the temperature T_5 consists of large number of small grains but that crystallized around the temperature T_4 consists of small number of large grains. Therefore, it seems that the glass number 1 crystallized at lower temperature (650 $^{\circ}$C) conforms to former case and that crystallized at higher temperature (750 $^{\circ}$C) conforms to the latter case. This may be confirmed by detailed study of the micro-structures of samples crystallized at various temperatures.

Surface roughness of 120 mesh is needed to induce electrically conducting layers on alkali containing silicate glasses by ion exchange and reduction method. Because surface roughness helps nucleation of surface droplets. However, in the present investigation it is found that ion exchange and

reduction method induces highly conducting layers on smooth surfaces ~~of~~ of roughness 1 micron of alkali containing silicate glass ceramic samples. Therefore, it appears that the crystals present in glass ceramic samples help nucleation of silver droplets. The glass crystal interface may be acting as nucleation sites as the interface reduces the free energy of activation for nucleation of silver droplets. This may be confirmed by electron microscopic study.

In the present investigation it is found that rough surfaces have higher conductivity and thicker conducting layers than smooth surfaces. This is possibly due to the fact that surface roughness also aids nucleation of silver droplets.

In case of glasses the TCR values of induced conducting layers are around 2000 ppm/$^{\circ}$K. But in case of glass ceramic samples of similar compositions the TCR values are found to be around 1000 ppm/$^{\circ}$K. In glass ceramic samples crystals are embedded in the film of silver droplets, making the film somewhat porous. This effect is not present in glass samples. This means that the conducting film in glasses is nearer to bulk silver than that of glass ceramic sample[2]. The crystals present in the film may be contributing some negative TCR leading to a reduction in the overall TCR value. A proper choice of crystal size and distribution in glass matrix may give still lower values. Rough surfaces of glass ceramic samples

are found to show higher TCR values than smooth surfaces. This may be due to the fact that in the former case more silver is formed due to surface roughness effect on nucleation of silver droplets.

Another interesting observation is that glass ceramic samples heat treated at lower temperatures (650 ^{o}C) are found to show very low surface resistance with positive TCR values. Whereas that heat treated at higher temperature (750 ^{o}C) is found to show higher resistance of the order 10^5 ohms/square with negative TCR. This is possibly due to continuous film in the former case and discontinuous film in the latter case. The exponential dependence of conductivity on 1/T of latter case also indicates the presence of discontinuous film. The linear dependence of conductivity on temperature with positive TCR in the former case indicates continuous film. This can be confirmed by electron microscopic study. The larger number of small grains in the sample crystallized at lower temperature have large interface area which may be nucleating more silver droplets to give a continuous film. Whereas small number of large grains in the other case have smaller interface area which may be nucleating less droplets to give a discontinuous film. This may be confirmed by electron microscopic study of silver droplets in both cases.

Fig 24 - Rates of homogeneous nucleation and crystal growth in a viscous liquid.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

(1) Detailed micro-structural study of crystallization in the glasses used in present investigation may be made in order to have a better understanding of crystallization process.

(2) Electron microscopic studies may be done to confirm the fact that the glass crystal interface helps the nucleation of silver droplets.

(3) The electrical properties of the films may be studied as a function of size and volume per cent of crystals present in glass ceramics and Na^+ content, keeping all other experimental conditions constant. In this study it is likely that a material with low TCR may be struck.

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APPENDIX I

Resistance variation with temperature of NiO-Li$_2$O

ceramic sample

$$l = 0.3 \text{ cm}$$
$$b = 0.8 \text{ cm}$$
$$R_{20} = 0.1163 \text{ ohms}$$
$$\beta_{20} = 0.3101 \text{ ohms/square}$$
$$TCR = 3300 \text{ ppm/}^{\circ}K$$

Temperature $^{\circ}$C	V-I Characteristics		Resistance (ohms)
	Current (m Amp)	Voltage (m Volts)	
1	2	3	4
32	2	0.245	0.1218
	3	0.365	
	4	0.490	
	5	0.615	
	6	0.730	
	7	0.855	
	8	0.975	
55	2	0.260	0.1311
	3	0.395	
	4	0.525	
	5	0.650	
	6	0.785	
	7	0.915	
	8	1.050	
89	2	0.290	0.1439
	3	0.430	
	4	0.575	
	5	0.720	
	6	0.865	
	7	1.010	
	8	1.150	

1	2	3	4
116	2	0.310	0.1539
	3	0.460	
	4	0.615	
	5	0.775	
	6	0.925	
	7	1.080	
	8	1.230	
128	2	0.315	0.1580
	3	0.475	
	4	0.630	
	5	0.790	
	6	0.950	
	7	1.110	
	8	1.260	
118	2	0.310	0.1539
	3	0.460	
	4	0.615	
	5	0.770	
	6	0.925	
	7	1.080	
	8	1.230	
108	2	0.300	0.1464
	3	0.450	
	4	0.600	
	5	0.755	
	6	0.900	
	7	1.000	
	8	1.200	

1	2	3	4
60	2	0.265	0.1314
	3	0.395	
	4	0.530	
	5	0.665	
	6	0.790	
	7	0.920	
	8	1.055	
51.5	2	0.260	0.1288
	3	0.385	
	4	0.515	
	5	0.645	
	6	0.770	
	7	0.905	
	8	1.030	
42.5	2	0.250	0.1255
	3	0.375	
	4	0.500	
	5	0.630	
	6	0.755	
	7	0.880	
	8	1.000	
27	2	0.240	0.1193
	3	0.355	
	4	0.475	
	5	0.595	
	6	0.720	
	7	0.830	
	8	0.955	

APPENDIX II

Resistance variation with temperature of sample 1A1μ

$$l = 0.35 \text{ cm}$$

$$b = 0.55 \text{ cm}$$

$$R_{20} = 17.88 \text{ ohms}$$

$$\beta_{20} = 28.09 \text{ ohms/square}$$

$$TCR = 684 \text{ ppm/ }^{\circ}K$$

Temperature $^{\circ}C$	V-I Characteristics		Resistance (ohms)
	Current (m Amp)	Voltage (m Volts)	
34	0.2	3.620	18.12
	0.3	5.455	
	0.4	7.230	
	0.5	9.070	
	0.6	10.850	
	0.7	12.680	
	0.8	14.520	
10	0.2	3.665	17.80
	0.3	5.360	
	0.4	7.120	
	0.5	8.895	
	0.6	10.640	
	0.7	12.455	
	0.8	14.240	
-10.5	0.2	3.540	17.52
	0.3	5.295	
	0.4	7.120	
	0.5	8.750	
	0.6	10.520	
	0.7	12.220	
	0.8	13.975	

1	2	3	4
−20	0.2	3.485	17.40
	0.3	5.210	
	0.4	6.960	
	0.5	8.700	
	0.6	10.440	
	0.7	12.175	
	0.8	13.925	
−34	0.2	3.470	17.24
	0.3	5.160	
	0.4	6.920	
	0.5	8.610	
	0.6	10.360	
	0.7	12.090	
	0.8	13.760	
−56	0.2	3.425	17.02
	0.3	5.125	
	0.4	6.760	
	0.5	8.435	
	0.6	10.745	
	0.7	11.790	
	0.8	13.460	
−67	0.2	3.380	16.82
	0.3	5.070	
	0.4	6.715	
	0.5	8.390	
	0.6	10.130	
	0.7	11.790	
	0.8	13.430	

1	2	3	4
−84	0.2	3.350	16.59
	0.3	5.000	
	0.4	6.640	
	0.5	8.350	
	0.6	9.980	
	0.7	11.600	
	0.8	13.210	
−98	0.2	3.300	16.45
	0.3	4.980	
	0.4	6.575	
	0.5	8.225	
	0.6	9.850	
	0.7	11.490	
	0.8	13.170	
−114	0.2	3.260	16.24
	0.3	4.860	
	0.4	6.560	
	0.5	8.125	
	0.6	9.740	
	0.7	11.380	
	0.8	12.960	
−129.5	0.2	3.225	16.10
	0.3	4.840	
	0.4	6.460	
	0.5	8.080	
	0.6	9.615	
	0.7	11.290	
	0.8	12.850	

1	2	3	4
−133	0.2	3.200	16.06
	0.3	4.840	
	0.4	6.440	
	0.5	8.030	
	0.6	9.625	
	0.7	11.240	
	0.8	12.850	
−106	0.2	3.265	16.33
	0.3	4.900	
	0.4	6.530	
	0.5	8.165	
	0.6	9.795	
	0.7	11.430	
	0.8	13.065	
−74	0.2	3.335	16.67
	0.3	5.035	
	0.4	6.675	
	0.5	8.345	
	0.6	1c.015	
	0.7	11.685	
	0.8	13.350	
−35	0.2	3.450	17.25
	0.3	5.175	
	0.4	6.905	
	0.5	8.620	
	0.6	10.350	
	0.7	12.075	
	0.8	13.800	

1	2	3	4
−16	0.2	3.475	17.38
	0.3	5.215	
	0.4	6.950	
	0.5	8.690	
	0.6	10.430	
	0.7	12.165	
	0.8	13.905	
+15	0.2	3.555	17.77
	0.3	5.330	
	0.4	7.110	
	0.5	8.885	
	0.6	10.660	
	0.7	12.440	
	0.8	14.215	

APPENDIX III

Resistance variation with temperature of sample 1A600

$$l = 0.5 \text{ cm}$$

$$b = 0.85 \text{ cm}$$

$$R_{20} = 0.4315 \text{ ohms}$$

$$\beta_{20} = 0.7336 \text{ ohms/square}$$

$$TCR = 1324 \text{ ppm/}^\circ K$$

Temperature $^\circ C$	V-I Characteristics		Resistance (ohms)
	Current (m Amp)	Voltage (m Volts)	
1	2	3	4
32.5	2	0.900	0.4463
	3	1.350	
	4	1.795	
	5	2.235	
	6	2.680	
	7	3.120	
	8	3.560	
16	2	0.875	0.4344
	3	1.300	
	4	1.745	
	5	2.175	
	6	2.600	
	7	3.050	
	8	3.465	

1	2	3	4
−1	2	0.840	0.4205
	3	1.275	
	4	1.690	
	5	2.115	
	6	2.525	
	7	2.940	
	8	3.350	
−9.5	2	0.830	0.4140
	3	1.260	
	4	1.660	
	5	2.085	
	6	2.440	
	7	2.905	
	8	3.320	
−14.5	2	0.825	0.4124
	3	1.240	
	4	1.650	
	5	2.070	
	6	2.480	
	7	2.880	
	8	3.295	
−27	2	0.810	0.4045
	3	1.215	
	4	1.620	
	5	2.030	
	6	2.435	
	7	2.830	
	8	3.225	

1	2	3	4
−35.5	2	0.810	0.3997
	3	1.195	
	4	1.600	
	5	2.005	
	6	2.390	
	7	2.795	
	8	3.200	
−49.5	2	0.795	0.3906
	3	1.180	
	4	1.560	
	5	1.960	
	6	2.340	
	7	2.725	
	8	3.125	
−63	2	0.775	0.3835
	3	1.155	
	4	1.700	
	5	1.915	
	6	2.290	
	7	2.670	
	8	3.005	
−72	2	0.755	0.3789
	3	1.140	
	4	1.520	
	5	1.900	
	6	2.275	
	7	2.645	
	8	3.030	

1	2	3	4
−82.5	2	0.750	0.3732
	3	1.130	
	4	1.490	
	5	1.870	
	6	2.240	
	7	2.605	
	8	2.985	
−95	2	0.740	0.3667
	3	1.100	
	4	1.470	
	5	1.840	
	6	2.200	
	7	2.570	
	8	2.925	
−107	2	0.720	0.3596
	3	1.070	
	4	1.440	
	5	1.795	
	6	2.170	
	7	2.520	
	8	2.870	
−116	2	0.710	0.3578
	3	1.075	
	4	1.430	
	5	1.785	
	6	2.130	
	7	2.485	
	8	2.895	

1	2	3	4
−129	2	0.700	0.3497
	3	1.055	
	4	1.405	
	5	1.745	
	6	2.100	
	7	2.450	
	8	2.790	
−138.5	2	0.685	0.3432
	3	1.040	
	4	1.365	
	5	1.715	
	6	2.060	
	7	2.410	
	8	2.740	
−105	2	0.725	0.3625
	3	1.090	
	4	1.450	
	5	1.810	
	6	2.175	
	7	2.540	
	8	2.900	
−68	2	0.770	0.3856
	3	1.150	
	4	1.535	
	5	1.920	
	6	2.305	
	7	2.685	
	8	3.070	

1	2	3	4
−20	2	0.815	0.4068
	3	1.220	
	4	1.630	
	5	2.035	
	6	2.440	
	7	2.850	
	8	3.255	
+7	2	0.855	0.4261
	3	1.280	
	4	1.705	
	5	2.133	
	6	2.560	
	7	2.985	
	8	3.410	

APPENDIX IV

Resistance variation with temperature of sample 2A1μ

l = 0.15 cm

b = 0.95 cm

R_{20} = 0.121 ohm

β_{20} = 0.766 ohm/square

TCR = 985 ppm/$^{\circ}$K

Temperature $^{\circ}$C	V-I Characteristics		Resistance (ohms)
	Current (m Amp)	Voltage (m Volts)	
1	2	3	4
40	2	0.245	0.1250
	3	0.370	
	4	0.490	
	5	0.615	
	6	0.790	
	7	0.860	
	8	0.985	
87	2	0.255	0.1282
	3	0.385	
	4	0.510	
	5	0.640	
	6	0.770	
	7	0.895	
	8	1.025	

1	2	3	4
129	2	0.265	0.1330
	3	0.400	
	4	0.535	
	5	0.665	
	6	0.800	
	7	0.930	
	8	1.065	
179	2	0.275	0.1389
	3	0.415	
	4	0.555	
	5	0.695	
	6	0.830	
	7	0.970	
	8	1.110	
201	2	0.285	0.1418
	3	0.425	
	4	0.575	
	5	0.710	
	6	0.855	
	7	0.995	
	8	1.135	
223	2	0.300	0.1445
	3	0.445	
	4	0.585	
	5	0.725	
	6	0.865	
	7	1.005	
	8	1.150	

1	2	3	4
198	2	0.295	0.1425
	3	0.430	
	4	0.575	
	5	0.720	
	6	0.850	
	7	0.995	
	8	1.135	
171	2	0.290	0.1391
	3	0.425	
	4	0.565	
	5	0.695	
	6	0.830	
	7	0.970	
	8	1.110	
161	2	0.290	0.1374
	3	0.420	
	4	0.550	
	5	0.685	
	6	0.830	
	7	0.960	
	8	1.090	
145	2	0.280	0.1357
	3	0.415	
	4	0.550	
	5	0.680	
	6	0.815	
	7	0.945	
	8	1.080	

1	2	3	4
128	2	0.275	0.1340
	3	0.410	
	4	0.540	
	5	0.675	
	6	0.805	
	7	0.935	
	8	1.065	
110	2	0.270	0.1318
	3	0.400	
	4	0.530	
	5	0.665	
	6	0.790	
	7	0.920	
	8	1.050	
97	2	0.270	0.1298
	3	0.400	
	4	0.525	
	5	0.655	
	6	0.775	
	7	0.900	
	8	1.035	
77.5	2	0.265	0.1274
	3	0.390	
	4	0.515	
	5	0.640	
	6	0.765	
	7	0.890	
	8	1.010	

1	2	3	4
63	2	0.262	0.1260
	3	0.385	
	4	0.510	
	5	0.635	
	6	0.755	
	7	0.880	
	8	1.000	
53.5	2	0.255	0.1249
	3	0.385	
	4	0.505	
	5	0.630	
	6	0.750	
	7	0.870	
	8	0.990	
43.5	2	0.260	0.1239
	3	0.380	
	4	0.500	
	5	0.625	
	6	0.740	
	7	0.865	
	8	0.985	
30	2	0.255	0.1223
	3	0.380	
	4	0.495	
	5	0.615	
	6	0.735	
	7	0.850	
	8	0.970	

APPENDIX V

Resistance variation with temperature of sample 2A600

$$l \; = \; 0.275 \; cm$$

$$b \; = \; 0.8 \; cm$$

$$R_{20} \; = \; 0.0924 \; ohm$$

$$\beta_{20} \; = \; 0.268 \; ohm/square$$

$$TCR \; = \; 1340 \; ppm/^{\circ}K$$

Temperature $^{\circ}C$	V-I Characteristics		Resistance (ohms)
	Current (m Amp)	Voltage (m Volts)	
1	2	3	4
48	2	0.190	0.09643
	3	0.285	
	4	0.385	
	5	0.480	
	6	0.575	
	7	0.670	
	8	0.770	
61	2	0.195	0.09804
	3	0.295	
	4	0.395	
	5	0.490	
	6	0.590	
	7	0.685	
	8	0.785	

1	2	3	4
92	2	0.205	0.1018
	3	0.305	
	4	0.410	
	5	0.510	
	6	0.610	
	7	0.715	
	8	0.815	
110	2	0.210	0.1039
	3	0.315	
	4	0.420	
	5	0.520	
	6	0.625	
	7	0.730	
	8	0.835	
140	2	0.215	0.1075
	3	0.320	
	4	0.430	
	5	0.535	
	6	0.645	
	7	0.750	
	8	0.860	
167	2	0.230	0.1104
	3	0.340	
	4	0.450	
	5	0.555	
	6	0.662	
	7	0.770	
	8	0.875	

1	2	3	4
151	2	0.230	0.1084
	3	0.335	
	4	0.440	
	5	0.545	
	6	0.650	
	7	0.755	
	8	0.860	
143	2	0.225	0.1076
	3	0.332	
	4	0.435	
	5	0.540	
	6	0.645	
	7	0.750	
	8	0.855	
132	2	0.225	0.1061
	3	0.325	
	4	0.430	
	5	0.535	
	6	0.637	
	7	0.740	
	8	0.840	
121	2	0.225	0.1052
	3	0.325	
	4	0.427	
	5	0.530	
	6	0.630	
	7	0.730	
	8	0.835	

1	2	3	4
110	2	0.220	0.1036
	3	0.320	
	4	0.425	
	5	0.520	
	6	0.620	
	7	0.720	
	8	0.822	
100	2	0.215	0.1025
	3	0.317	
	4	0.415	
	5	0.515	
	6	0.610	
	7	0.715	
	8	0.817	
87.5	2	0.215	0.1008
	3	0.312	
	4	0.410	
	5	0.510	
	6	0.600	
	7	0.700	
	8	0.800	
78	2	0.212	0.09992
	3	0.305	
	4	0.405	
	5	0.500	
	6	0.600	
	7	0.695	
	8	0.795	

1	2	3	4
65.5	2	0.210	0.09894
	3	0.300	
	4	0.400	
	5	0.495	
	6	0.590	
	7	0.690	
	8	0.790	
59	2	0.202	0.09704
	3	0.300	
	4	0.395	
	5	0.490	
	6	0.580	
	7	0.675	
	8	0.770	
50	2	0.205	0.09635
	3	0.295	
	4	0.395	
	5	0.485	
	6	0.575	
	7	0.670	
	8	0.765	
42.5	2	0.200	0.09495
	3	0.290	
	4	0.387	
	5	0.482	
	6	0.570	
	7	0.660	
	8	0.750	

1	2	3	4
34	2	0.200	0.0939
	3	0.290	
	4	0.382	
	5	0.470	
	6	0.565	
	7	0.652	
	8	0.745	
27	2	0.200	0.09267
	3	0.285	
	4	0.377	
	5	0.465	
	6	0.555	
	7	0.645	
	8	0.735	

APPENDIX VI

Resistance Variation with Temperatures of Sample 1B600

$$l = 0.3 \text{ cm}$$

$$b = 0.83 \text{ cm}$$

$$R_{20} = 1.285 \times 10^5 \text{ ohms}$$

$$\rho_{20} = 3.55 \times 10^5 \text{ ohms/square}$$

TCR (at room Temperature) $= -4340 \text{ ppm/}^\circ\text{K}$

Activation Energy (E) $= 1.04 \times 10^{-13} \text{ ergs.}$

Temperature ($^\circ C$)	$\dfrac{10^3}{T^\circ K}$	V-I Characteristics		Resistance (10^5 ohms)	Conductivity (σ) (10^{-5} ohm^{-1})	Log
		Current (10^{-5} Amp)	Voltage (Volts)			
1	2	3	4	5	6	7
185	2.18	1	0.55	0.5525	1.81	-4.74
		1.5	0.83			
		2	1.12			
		2.5	1.4			
		3	1.7			
		3.5	1.92			
		4	2.2			
167	2.27	1	0.62	0.615	1.63	-4.78
		1.5	0.92			
		2	1.23			
		2.5	1.53			
		3	1.85			
		3.5	2.16			
		4	2.47			
154.5	2.34	1	0.65	0.64	1.565	-4.80
		1.5	0.97			
		2	1.3			
		2.5	1.6			
		3	1.9			
		3.5	2.24			
		4	2.55			

1	2	3	4	5	6	7
142	2.41	1.5	1.03	0.68	1.47	−4.832
		2	1.37			
		2.5	1.7			
		3	2.03			
		3.5	2.4			
		4	2.7			
130	2.48	1.5	1.1	0.725	1.38	−4.860
		2	1.45			
		2.5	1.82			
		3	2.18			
		3.5	2.55			
		4	2.9			
117.5	2.56	1.5	1.15	0.77	1.30	−4.885
		2	1.53			
		2.5	1.92			
		3	2.3			
		3.5	2.7			
		4	3.08			
102	2.67	1.5	1.27	0.84	1.19	−4.924
		2	1.68			
		2.5	2.1			
		3	2.5			
		3.5	2.95			
		4	3.35			
87.5	2.78	1.5	1.38	0.9	1.1	−4.954
		2	1.8			
		2.5	2.26			
		3	2.7			
		3.5	3.16			
		4	3.6			
74	2.88	1.5	1.5	0.975	1.025	−4.989
		2	1.96			
		2.5	2.44			
		3	2.9			
		3.5	3.4			
		4	3.9			

-589

1	2	3	4	5	6	7
60	3.00	1	1.1	1.06	0.945	−5.024
		1.5	1.6			
		2	2.15			
		2.5	2.66			
		3	3.18			
		3.5	3.7			
		4	4.22			
47	3.12	1	1.15	1.135	0.880	−5.055
		1.5	1.7			
		2	2.26			
		2.5	2.84			
		3	3.4			
		3.5	3.94			
		4	4.56			
36.5	3.24	1	1.2	1.19	0.842	−5.075
		1.5	1.8			
		2	2.4			
		2.5	3			
		3	3.54			
		3.5	4.15			
		4	4.7			
46		1	1.13	1.125		
		1.5	1.69			
		2	2.25			
		2.5	2.81			
		3	3.36			
		3.5	3.94			
		4	4.5			
75		1	0.95	0.953		
		1.5	1.43			
		2	1.9			
		2.5	2.38			
		3	2.86			
		3.5	3.34			
		4	3.84			

1	2	3	4	5	6	7
103		1	0.8	0.8		
		1.5	1.2			
		2	1.6			
		2.5	2			
		3	2.4			
		3.5	2.8			
		4	3.2			
146		1	0.65	0.649		
		1.5	0.97			
		2	1.30			
		2.5	1.62			
		3	1.95			
		3.5	2.27			
		4	2.60			

APPENDIX VII

Resistance Variation with Thickness of Conducting Layer Removed

of Sample 1A1M

1 = 0.35 cm

b = 0.55 cm

Temperature of measurement = 34 °C

Thickness of conducting layer removed (microns)	V-I Characteristics		Resistance (ohms)
	Current (m Amp)	Voltage (m Volts)	
0	0.2	3.620	18.12
	0.3	5.455	
	0.4	7.230	
	0.5	9.070	
	0.6	10.850	
	0.7	12.680	
	0.8	14.520	
10	0.02	1.41	71
	0.03	2.15	
	0.04	2.85	
	0.05	3.56	
	0.06	4.30	
	0.07	5.01	
	0.08	5.67	
18	0.002	0.80	390
	0.003	1.14	
	0.004	1.55	
	0.005	1.94	
	0.006	2.37	
	0.007	2.76	
	0.008	3.11	
23			5×10^8

APPENDIX VIII

Resistance Variation with Thickness of Conducting Layers

Removed, of Sample 1A600

l = 0.5 cm

b = 0.85 cm

Temperature of Measurement = 32.5 °C

Thickness of conducting layer removed (microns)	V-I Characteristics		Resistance (ohms)
	Current (m Amp)	Voltage (m Volts)	
0	2	0.9	0.446
	3	1.35	
	4	1.795	
	5	2.235	
	6	2.68	
	7	3.12	
	8	3.56	
11	2	2.1	1
	3	3.05	
	4	4.01	
	5	5.0	
	6	6.0	
	7	7.0	
	8	8.0	
23	0.02	0.855	42
	0.03	1.26	
	0.04	1.52	
	0.05	2.05	
	0.06	2.58	
	0.07	2.94	
	0.08	3.28	
27	0.02	3.28	162
	0.03	4.92	
	0.04	6.52	
	0.05	8.05	
	0.06	9.72	
	0.07	11.27	
	0.08	12.96	
33			9.5×10^6
35			More than 10^9

APPENDIX IX

Programme for Computing Resistance Values by Least Square Fit

$$A = \frac{\Sigma\, X_i\, Y_i}{\Sigma\, X_i^{2}}$$

A – Resistance

X_i – Current

Y_i – Voltage

```
READ  ,N,(X(I),Y(I),I = 1,N)
XY = 0.0  XSQ = 0.0
DO 5 I=1,N
XY = XY + X(I)*Y(I)
5 XSQ = XSQ+X(I)**2
A = XY/XSQ
PRINT,A
```